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VOC Extraction from Softwood Through Low-Headspace Heating

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VOC Extraction from Softwood Through Low-Headspace Heating

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Summary

Volatile organic compounds (VOCs) released during wood drying face present or potential regulation. Two approaches are reported to control VOC release: heating green wood or irradiating it with microwave energy, both in a low-headspace environment. Heating green flakes (for OSB manufacture) in a low-headspace environment releases VOCs but proportionately much less water. Hence, it is feasible to extract and collect the VOCs from green wood prior to drying, and to then dry with lowered emissions. Irradiating flakes with microwave leads to contrasting behavior. Water is released with very little VOC loss if the flakes are microwaved in an open container. Microwaving under low-headspace conditions removes the VOCs, but retains the water in the wood. The water trapped in the wood because of the low-headspace restriction drives the VOCs out of the hydrophobic regions (*e.g.*, resin canals) where they are principally located into hydrophilic zones. Movement out of the hydrophilic environment and out of the wood is then quite rapid. Hence, either VOC or water release can be targeted by adjusting the headspace during microwaving. Most of the VOCs lost during drying originate from the surface, and low-headspace microwaving releases this surficial material. Hydrogen isotope exchange work shows that microwaving increases water access to the exchangeable protons in dry, or partially dry, wood tissue. Similar results are obtained with low-headspace radiofrequency (RF) irradiation of lumber. The terpenes are carried out with the small amount of steam generated. RF treatment does not induce a significant change in strength.

Keywords: microwave, radiofrequency, flakes, lumber, particle, pinene, terpene, VOC, low-headspace, recovery

Introduction

Environmental regulations in the United States impose controls on wood drying facilities. Regenerative Thermal Oxidation units (Yeo, 1993, Grzanka, 1996, Matros et al., 1996) are most often employed, but they are capital-intensive, and are associated with substantial operating and maintenance costs. CO₂ and NO_x emissions from the control units are additional negatives. The reliance on control devices would be minimized if emissions could be reduced through process changes. In previous papers, we outlined strategies for reducing VOCs by changing drying practices without adding significant new capital equipment (Banerjee et al., 1998, Su et al., 1998).

We now demonstrate the principle of a new process whereby softwood VOCs can be substantially recovered from wood prior to drying.

When green wood is heated in a low-headspace environment, energy is transferred to both wood tissue and the entrained water. Since most of the water is unable to leave because of the low-headspace restriction, its movement or rate of mixing within the wood matrix, should increase. Wood constituents that are at least partially soluble in water should also be better mixed as a result. Alexiou et al. (1990) have shown that pre-steaming under saturation conditions mobilizes Eucalyptus heartwood extractives, probably by allowing water greater access to cell walls. A similar effect should occur for turpentine in softwood, since the turpentine components are principally localized in specific hydrophobic regions in wood (resin canals). Low-headspace heating should even out their concentrations, and help move them to the surface, from which they can more easily leave the wood. As a result, some of the turpentine should be removed from green wood which can then be dried conventionally with reduced emissions. In this paper we apply this concept to the extraction of turpentine from softwood.

Description of the Experiments

The purpose of these experiments was to determine the suitability and efficacy of steam and dielectric heating in a low-headspace enclosure to remove terpenes from both wood particles and from lumber. The two methodologies are functionally dissimilar; unlike thermal (steam) heating where the heat moves from the surface of the wood to the interior, dielectric heating (e.g., microwave or RF heating) transfers energy to the entire wood matrix. The combination of particles and steam was attempted first. Loblolly pine particles and flakes were solicited from three mills in the southern U.S., wrapped in plastic and placed in cold storage for use within a few days. Unseasoned lumber was obtained and handled similarly.

Steaming Trials

Particles

Particles were steamed in the low-headspace cylinder, a 10.2 cm OD x 69 cm long sealed stainless steel vessel with a quick disconnect union at one end for sample loading and unloading. The cylinder accepts up to 100 g. of furnish, and is illustrated in Figure 1. Steam can be fed into the vessel at pressures from 1-3.5 atmospheres. The unit is fitted with a steam vortex meter with pressure and temperature outputs, needle valves to retain the steam in the vessel after injection, and a pressure relief valve. Heating tape is wrapped around the vessel to minimize condensation inside the cylinder. Steam times and temperatures were varied to determine whether these variables had any effect on VOC recovery; steaming times ranging from 15 to 60 minutes were used, and the steam temperatures ranged from 119 to 179°C. The steam was vented through a methanol trap to recover the VOCs.

The steamed particles were dried in a 3.8 cm diameter ceramic tube furnace at 130°C for 30 minutes. The furnish was placed in a ceramic boat in the center of the tube, a 3.8 cm midsection of which was electrically heated. To evaluate the completeness of VOC removal by the prior steaming operation, air was metered to the tube inlet at 2 lpm, and the furnace emissions were drawn into a JUM Model VE7 flame ionization analyzer (FIA) through its built-in pump. This unit is used in US EPA Method 25A for monitoring VOC emissions (Anonymous, 1995).

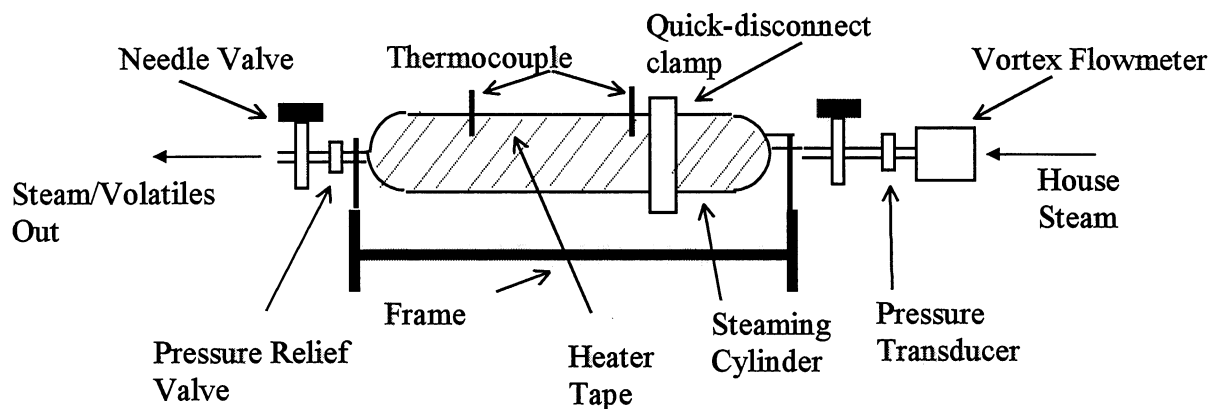


Figure 1: Schematic of a low-headspace steaming unit

Terpenes and resin acids were analyzed by GC-FID; the resin acids were derivatized by trimethylanilinium hydroxide prior to injection.

Lumber

To evaluate the feasibility of removing VOCs from lumber by steaming it in a low headspace environment, an experimental pilot-scale kiln (0.33 m³ capacity) at Mississippi State University was fitted with a steam spray. Two kiln runs were made with end-matched samples of southern pine. Wood (0.085 m³) with an average specific gravity of 0.42 was used for each run. One set was steamed for 5 hours (under saturation conditions) in a 0.42 m³ steamer, and then kiln-dried for 18 hours to a final moisture content of 6% on an oven-dry basis, while the other served as a control and was only kiln-dried. Steaming was done at 100°C; the kiln temperature was 118°C, and the wet-bulb temperature during drying was approximately 82°C, but was not controlled. Total hydrocarbon data were collected throughout the entire drying cycle. After steaming, the lumber was dried in the pilot kiln and the VOCs emitted during drying were measured by Method 25A.

Trials Using Dielectric Heating

Flakes

For each trial, three paired sets of flakes (2–3 g) were prepared by breaking individual pieces in half to form two equivalent furnish samples. One set from each pair was microwaved in a Teflon cylinder (4.4 cm diameter x 10.2 cm length) fitted with a screw cap containing a small opening that accommodated a fiber optic thermocouple. Damp sponge inserts were positioned at both ends of the cylinder to prevent moisture loss during treatment. Both microwaved and control flakes were subsequently dried similarly to the particles in the steaming experiment (in the tube furnace at 130°C). The microwave units used were a Panasonic NN-6405A oven, and a Corber Electronics, Dimension 3 system.

Lumber

Radiofrequency work was done with the Strayfield dryer located at Georgia Power's Technology Application Center in Atlanta, GA; the irradiation frequency was 27.12 MHz.

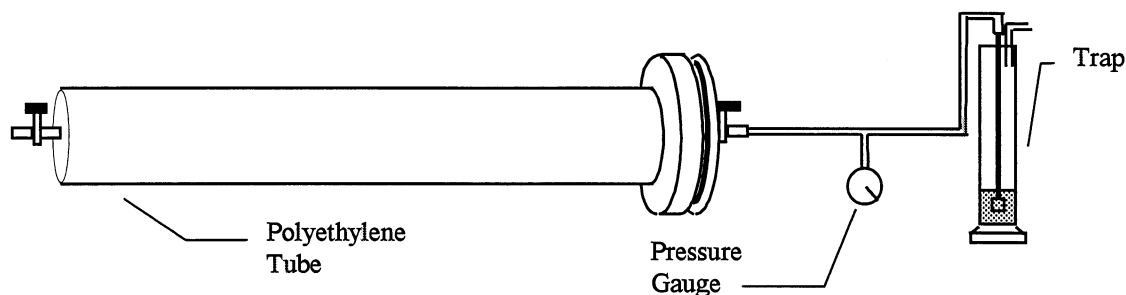


Figure 2: Schematic of a low-headspace unit for use in a RF dryer

For the first experiments, low-headspace conditions were achieved by simply wrapping the charge (nominal 50mm x 100 mm x 60cm pieces of southern pine) in plastic. These experiments demonstrated that approximately 50–60% of the VOCs could be removed during two- to six-minute RF treatment at 0.6A, but water loss was high at the longer treatment times, possibly due to leakage through the plastic wrapper. Confirmatory experiments using longer boards were run with the vessel shown in Figure 2. The unit is a 1.2 m. long by 11.4 cm OD polyethylene tube with a polyethylene flange heat-welded at one end and a plate welded at the opposite end. Teflon shutoff valves were installed at both ends. A trap containing water was connected to one end of the extraction vessel. Omega HHTFO-1 fiber optic thermocouples were used to determine the surface and internal temperatures of the charge during irradiation. The internal temperature was obtained by inserting the thermocouple into a pre-drilled hole in the wood, which reached the board centerline.

Pine boards (nominal 50mm x 100mm x 120 cm) were treated using RF energy under the following conditions: (i) 30 minutes of continuous RF treatment at 0.8 amps; (ii) 30 minutes of intermittent RF treatment at 1.1 amps, with the power being manually cycled on and off to maintain the surface temperature at just below 100°C; (iii) repetition of the above treatment for 15 minutes; and (iv) RF treatment until pressure built up in the vessel indicating the release of steam. For condition (i) the interior temperature increased linearly to about 100°C over 15 minutes and then held steady. The surface temperature climbed linearly to 100°C over 30 minutes.

Results

Extraction of VOCs through low-headspace steaming

Particle

VOCs from particles were measured during 30 minutes of drying, and the results are shown in Table 1. The difference in released VOCs between the control and the steamed flakes reflects the VOCs removed during steaming. Compared to the control samples, over 45% of the VOCs were removed during steaming at high temperature (>150°C). Increasing the steaming time from 30 to 60 minutes did not increase the VOCs extracted to any substantial extent, but the furnish turned noticeably darker. Lower amounts of VOCs were extracted during low-temperature steaming.

The final column in Table 1 is the pinene recovered in the methanol trap as a percentage of total VOC lost from the wood as measured by Method 25A. Although Method 25A measures

Table 1: VOC emissions from drying steamed particle¹				
<i>high temperature steaming</i>				
steam time (min)	steam temp (°C)	VOC (µg/g, dry basis)	n	VOC recovered in the trap(%)²
0 (control)		1300 ± 200	8	
15	174	580 ± 30	4	470
30	179	490 ± 10	4	549
30	174	510 ± 40	4	454
30	178	690 ± 30	4	221
30	152	720 ± 80	3	
60	172	490 ± 80	4	372
60	178	510 ± 40	4	
<i>low temperature steaming</i>				
30	119	830 ± 10	4	18
30	122	810 ± 50	4	12
¹ at 130°C for 30 minutes; ² n=1; measured by gc				

all the VOCs emitted during drying, pinene is the major VOC constituent (Cronn et al., 1983). The VOC recovery from steaming was lower than anticipated, probably because of material left in the vessel. A subsequent experiment was conducted to investigate the effect of re-steaming on VOC emissions. Once-steamed particles were steamed at 179°C for 30 minutes, allowed to cool, and then re-steamed for another 30 minutes at 173°C. The wood was then dried in the tube furnace. Although 80% of the VOCs was recovered during steaming, as compared to the control, the particles darkened after the second steam treatment.

The above experiments were conducted under pressure since the steam was introduced under atmospheric pressure, and the sealed unit was then heated. To separate the effects of temperature and pressure, particles were steamed at about 167°C for 10 minutes under sealed conditions (with the valve closed), and then for 20 minutes with the needle valve cracked slightly open. The steamed wood was then heated in the tube furnace for 30 minutes at 130°C, and the VOCs measured. Substantial VOC (73%) loss occurred during steaming. Runs were also made where the needle valve was partially opened immediately after the vessel was charged with steam, *i.e.*, the material was steamed continuously at atmospheric pressure. Sixty seven percent VOC removal was realized. These results demonstrate that high temperature, and not high pressure, is the key to VOC extraction, and that steaming particles at elevated temperature is a viable means of extracting

Lumber

Two VOC emission peaks are usually observed when wood is dried. The first peak is associated with near-surface VOCs. Later, when drying is quite advanced and the wood is no longer evaporatively cooled, the temperature rises and mobilizes the VOCs in the interior to give rise to the second peak (Banerjee et al., 1995). The level of VOC emissions from the control

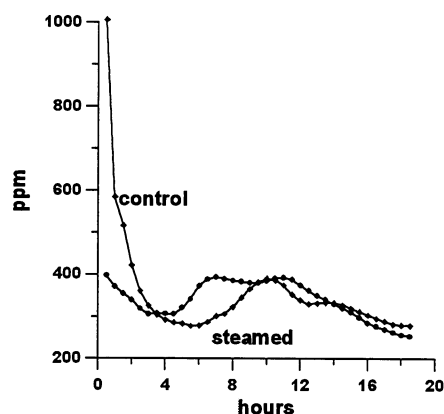


Figure 3: VOCs from control and steamed lumber

material used in this experiment was typical, with the VOC surges occurring when expected. The profile from the control essentially lagged that of the steamed material by about 2 hours. Total hydrocarbon data collected during the 18-hour kiln cycles are illustrated in Figure 3. Steaming reduced the area of the initial peak much more than it did the second (later) peak, indicating that the VOCs closer to the surface are preferentially removed by this procedure. Emissions from the control lumber were 1.5 $\mu\text{g/g}$ (dry basis), and emissions from the pre-steamed/kiln-dried material were 1.4 $\mu\text{g/g}$ (dry basis). Although steaming lowered the total hydrocarbon emissions, less than 10% of the total VOCs were removed from the lumber; considering the increased kiln residence time required, this reduction is too small for the process to be commercially viable.

Extraction of VOCs through low-headspace microwaving

Flakes

The VOCs released during drying (Method 25A) are compared in Table 2. Clearly, emissions from the microwaved wood are greatly reduced. Hence, brief microwaving under low-headspace conditions extracts much of the VOCs while retaining the water in the wood. As observed with steam, microwaving reduces the intensity of the initial VOC signal, indicating that the VOCs closest to the surface are preferentially removed.

Trials in which microwaving was attempted under open conditions, *i.e.* without the low-headspace restriction, resulted in the loss of water, but the VOCs were mostly retained in the wood. Since the major difference between the low-headspace and the open experiments is the retention of water in wood in the former, water must assist VOC removal under low-headspace conditions. Simply put, the hot water confined in the wood by the low-headspace constraint promotes VOC release from wood. Water strongly absorbs microwave energy, whereas energy absorption by wood is much weaker, *i.e.*, dry wood is not a lossy material. We hypothesize that without the headspace limitation, the water or steam moves quickly out of the flake before it is able to extract the VOCs from the wood. Hence, either VOC or water release can be selected by keeping the headspace open or closed. We do not imply that VOCs can only be removed through interaction with water; simple evaporation must also be a mechanism.

Table 2: VOC emissions from microwaved wood¹	
microwave conditions	VOC (µg/g) (green basis)
control	536
600 W, 3 min.	329
control	857
1200 W, 1 min.	145
control	767
1200 W, 1 min.	266
¹ at 130°C over 60 minutes	

Table 3: VOC emissions at 130°C drying (over 60 minutes)			
microwave treatment	boiling water treatment	weight loss (%)	VOC (µg/g) (green basis)
600 W, 2 min.	n/a	47.70	239
	5 min.	45.84	352
600 W, 2 min.	n/a	35.66	424
	5 min.	38.35	799
600 W, 2 min.	n/a	41.41	215
	5 min.	38.62	514

To ensure that the better performance of the microwave treatment was not just due to a higher flake temperature, one of a paired set of flakes was microwaved, and the other was immersed in boiling water. A thermocouple was placed inside the Teflon cylinder for the boiling water experiments, and the temperature was monitored continuously. For the microwave work the temperature was taken just after microwaving. Preliminary experiments demonstrated that the flakes reached about 90°C after either 5 minutes immersion in boiling water or 2 minutes microwaving at 600 watts. Both sets were then dried and their VOCs measured. The comparison in Table 3 demonstrates that more VOCs are released during microwaving. Hence, the decrease in VOCs during drying shown in Tables 2 and 3 are induced by the microwave irradiation, and not just by the attendant increase in temperature. The temperature and pressure gradients created by microwaving possibly increase the internal mixing of water to promote VOC release.

Table 4: VOCs from RF-treated lumber¹				
ID	RF time/total time (min)	RF power (amp)	weight loss (%)	VOC (µg/g)
control	0	na	na	1.52
C	30/30	0.8	2.8	0.69
F	12/30	1.1	4.0	0.32
H	12/15	1.1	3.8	0.75
A	9/9	1.1	2.2	0.94
¹ green basis				

Lumber

Table 4 summarizes the results from the drying runs conducted at different time and power combinations. The *RF time* reflects the actual irradiation time, while the *total time*, includes the additional period the wood was kept in the cylinder, regardless of whether or not the RF unit was on. The VOC profiles illustrated in Figure 4 clearly illustrate the potential for VOC reduction available through RF-pretreatment.

Entries F and H in Table 4 received the same amount of radiation (12 minute exposures) but the former was kept in the unit for 30 minutes instead of 15 minutes, and the wood was consequently exposed to saturated headspace conditions for a longer period. Not surprisingly, increasing power (compare C and F) and exposure period (H and A) increased the amount of VOCs removed. VOC reduction of 79% was observed in the best case (F). Importantly, this was achieved with minimal water loss, which opened the possibility of driving out and collecting VOCs through low-headspace RF treatment and then drying the wood conventionally with much lower releases. The power requirement should be quite low since the RF field is not used to evaporate water, but only to maintain the wood at a set temperature.

Mechanism of microwave-induced VOC release from wood

The VOCs lost from wood maintained under low-headspace conditions under a microwave field originate from the periphery of the furnish. Consider the profiles in Figure 5, which correspond to the first pair of entries in Table 2 (microwaved at 600 W for 3 minutes). Note that the reduction in VOCs for the microwaved wood occurs early in the process. The first VOC peak reflects surficial material, which is released when the wood is initially heated (Banerjee et al., 1995). The second broader band arises when the wood is mostly dry, and originates from the interior of the furnish. The wood dries in approximately 25 minutes in the Figure 5 experiment, *i.e.*, during the rise of the second peak. Since microwaving affects this second signal minimally, if at all, it is clear that only the surface VOCs are released during microwaving. Much of the mass in a piece of wood resides near the surface. For example, consider a cube of length l . Its volume is then l^3 . The volume of wood lying within a distance of $0.1 l$ of the surface is $0.49 l^3$. Hence, depending upon the sample dimensions, the “surface” can represent a large proportion of the wood.

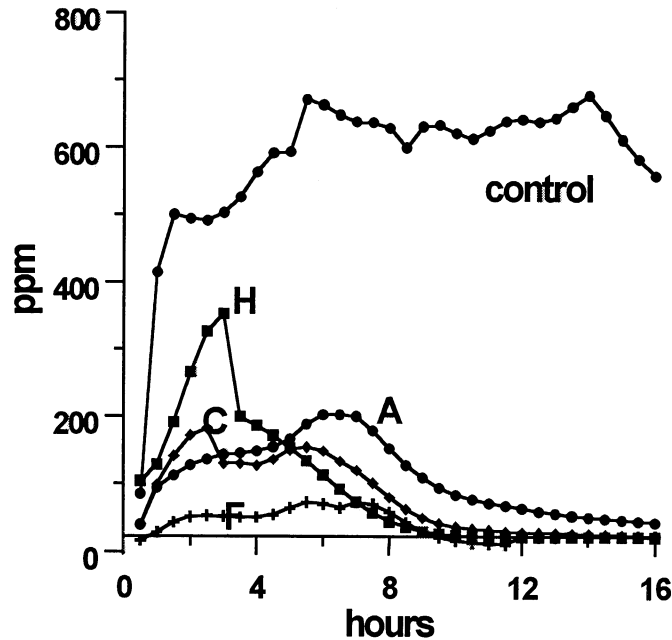


Figure 4: VOCs from low-headspace RF-treated lumber

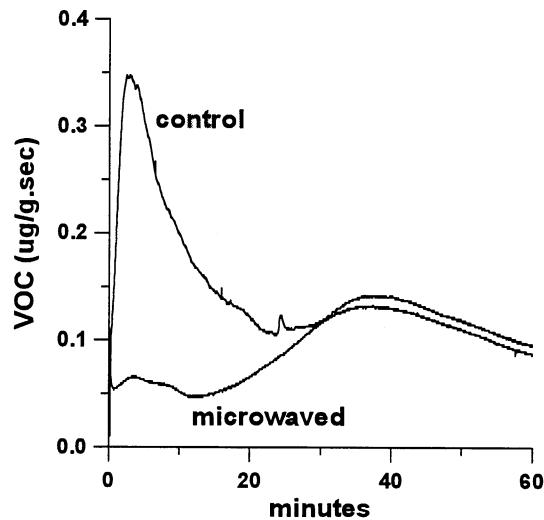


Figure 5: VOC profiles from control and microwaved OSB flakes

Collection of VOCs from low-headspace RF treatment of lumber

A preliminary experiment was conducted to determine the quantity and purity of turpentine that could be separated during the RF operation. Eight 2 x 3.25 x 22" pieces of loblolly pine were treated by RF (30 minutes, 0.9A) within two days of collection at the mill, with the emissions being collected in a cold water trap. Our low-headspace vessel can only accommodate one board at a time, so each board was irradiated individually with the same trap being used to

Table 5: Analysis of trapped emissions and condensate/rinsate				
	α-pinene ($\mu\text{g/g}^1$)	β-pinene ($\mu\text{g/g}^1$)	total VOCs ($\mu\text{g/g}^1$)	total resin acids ($\mu\text{g/g}^1$)
trapped emissions	250	187	518	0
condensate/rinsate	0.45	0.46	6.4	520 ²
¹ green basis, analysis by gc; ² resin acid distribution: pimaric (5%); unknown (17%); isopimaric (28%); dehydroabietic (9%); abietic (27%); neoabietic (14%)				

collect all the emissions. A total of 8.4 g. of turpentine was found floating on the surface of the water trap, which corresponds to 1.1 $\mu\text{g/g}$ (dry basis). Pinene represented 92% of the material.

To better define the efficiency of VOC collection from the headspace, the trap in Figure 2 was filled with 250 mL of methanol in an ice bath. Lumber (2.7 kg., 4.4 x 8.3 x 112 cm) was irradiated in the Strayfield dryer at 1.1 amps with cycling to keep the external wood temperature at about 100°C. The wood was removed after 30 minutes of irradiation, the condensed steam inside the vessel was collected, and the vessel was then rinsed with 250 mL of methanol. The material trapped in methanol was released during irradiation, and the VOCs in this fraction are referred to as *trapped emissions* in Table 5. The condensate and rinsate are collectively called *condensate/rinsate*. The milky condensate/rinsate was clarified through addition of a 1:1 methanol: ether solution. Most of the terpenes (about 0.4 $\mu\text{g/g}$, green basis) were found in the trapped emissions. While this is by no means optimized, it is roughly comparable to the difference between the control and RF-treated values in Table 4. Hence, much of the VOCs removed from wood by RF are recoverable.

Effect of RF-irradiation on strength

Twenty five 3.8 cm x 14 cm x 244 cm (nominal 2" x 6" x 8") southern pine boards were machined into 10 cm (4")-wide pieces, and further cut in half into side-matched pairs. One of the paired pieces was irradiated (but not dried) with RF (taking 40 minutes to reach 100°C), while the other served as a control. Both sets were subsequently dried using a conventional temperature-time based schedule to a final average MC of 15%. After drying, the lumber was equilibrated to about 12% MC. Two boards from each charge warped during drying and were not tested. Twenty-three pairs of specimens were tested for compression, shear, and bending; due to the greater variability expected in testing small cross-sections of southern pine, two groups of 23 specimen pairs were tested in tension, and 51 toughness specimens (equally divided between radial and tangential tests) were also tested per treatment.

Because the material to be tested was commercial-size lumber, it was not possible to use the ASTM standard D 143-specified specimen dimensions for all the tests; for example, the standard specifies the use of 2" x 2" x 30" bending specimens (28" span), but the surfaced and dried lumber was only 1.5" thick. Therefore, the reduced specimen sizes formerly incorporated into the National Forest Products Association's National Design Specification (Appendix Q, National Forest Products Association, 1986) were used. Appendix Q was originally written to standardize tests of fire-retardant-treated dimension lumber, and specimen dimensions are as similar to D 143's intentions as possible but recognize the limitations of the reduced cross-sectional area

available. In the case of the bending specimens, for example, the ASTM-prescribed 14:1 span-to-depth ratio is maintained through the use of a 21" span with a 23" specimen.

Specimen data were first tested for normality using the Shapiro-Wilk test at $\alpha=0.05$, then used to test the null hypothesis that there were no differences between control and RF-treated specimens using paired two-sided t-tests with $\alpha=0.5$. One group of tension specimens had a p-value less than 0.05, so the paired two-sample Wilcoxon signed rank test was used in place of the t-test for this group. The null hypothesis was not rejected for the following tests: modulus of elasticity, compression, tension, shear and toughness. The modulus of rupture results proved to be different for the two sets of data; the group of RF-treated specimens had MOR values approximately 90% of the control group. We conclude that RF treatment does not significantly affect mechanical properties, but in view of the apparent reduction in MOR a study with a larger sample size would be prudent.

Effect of microwaving on wood structure

Green pine blocks (5 x 2.5 x 2.5 cm) were dried to different moisture levels at 120°C, immersed in D₂O (>99% isotopic content) at room temperature for the periods shown in Table 6, and were then cut in halves. One half was wrapped in plastic and microwaved at 110 W for 30 minutes, until the internal temperature (as measured by a fiber-optic thermometer) reached 100°C. The field was then shut off for 15 minutes, and the cycle was repeated until the wood experienced 30 minutes of actual microwaving. The wrap retained the water in the wood. The other half of the soaked wood served as a control. Fibers taken from just inside the wet surface from five regions along the length of the piece were then analyzed by mass spectrometry with a direct insertion probe. The ion chromatograms of the three isotopic forms of water, namely H₂O, HOD, and D₂O, were parallel to one another as the wood was heated inside the spectrometer. In other words, the H₂O: HOD: D₂O proportion remained constant throughout, indicating that all three forms of water were bound equally strongly to the wood, and that fractional distillation did not occur.

The water released from the green wood (MC: 125%) had the same isotopic composition regardless of whether or not the wood was microwaved (Table 6), indicating that the exchangeable protons in green wood were not affected by microwaving. However, with the use of progressively drier wood, the water released from fibers taken from the microwaved wood was of lower isotopic content, which means that isotope exchange occurred to a larger degree. Presumably, microwaving opened up the wood structure and increased access of D₂O to the exchangeable protons in wood tissue. The exchangeable protons in dried wood are mostly those situated on hydroxyl groups, and the difference in isotopic exchange is the greatest for the dried wood. This suggests that most of the protons in green wood are exchangeable with the isotope under ambient conditions; i.e. the wood structure is open. As the wood dries, internal hydrogen bonding restricts access of the D₂O to some of the hydroxyl protons. It would seem that the energy transferred to water upon microwaving is sufficient to, at least partially, overcome this barrier. The effect resembles the hysteresis that occurs for moisture sorption to green and dried wood. Analogous isotope exchange work with D₂O has been previously conducted (Bikales and Segal, 1971, Gordeev et al, 1991, Jeffries, 1964, Kamide et al, 1984, Krassig, 1977, 1979, 1984, Mann and Marrian, 1956) to determine the accessibility of water to cellulose.

Table 6: Isotopic content of water released from wood			
MC (%) ¹	soaking period (days)	percent deuterium (σ) ²	
		control	microwaved
125	5	48 (15)	47 (8)
44	10	56 (16)	47 (5)
24	2	60 (4)	49 (7)
0	5	61 (7)	45 (3)
¹ dry basis MC of the wood being microwaved; ² averaged from 5 samples			

Discussion and Conclusions

Energy transferred to water constrained in wood is probably dissipated through thermal motion of the water within the wood matrix. The isotopic work illustrates this quite well; under irradiation, D₂O is able to access hydrogen-bonded areas in partially dried wood that are otherwise excluded. The contrast between open and low-headspace microwaving demonstrates that hot water, when forced to remain in the wood through the low-headspace restriction, aids in removing the VOCs out of wood. Thus, there must be at least two means of VOC removal from wood during conventional drying. Water must be at least partially responsible for VOC loss from green wood during early drying. VOC removal from dry wood must be driven by vapor pressure considerations (Banerjee et al. 1995, 1998).

The VOC material is concentrated in hydrophobic regions within the wood matrix. We believe that transferring energy to water while constraining it to remain in the wood promotes transport of the VOCs to hydrophilic zones from which they can rapidly move out of wood. Alexiou et al. (1990) have shown that pre-steaming *Eucalyptus* mobilizes heartwood extractives, probably by allowing water greater access to cell walls. Irradiating wood under low-headspace conditions appears to promote this access. Also, the sapwood is likely to heat up more rapidly than heartwood during microwaving owing to its higher water content, and the resulting temperature and pressure gradients may promote mixing.

The physics of VOC removal is not presently known, and is under study. However, the only apparent difference between VOC extraction through steaming and microwaving is that the latter occurs much more quickly. Since water absorbs microwave energy much more easily than does wood, the wood is principally heated by the water, and the wood-water interaction should, therefore, be more closely coupled during microwaving (or RF-treatment), than during steaming. This, in turn, should transfer more VOC material into the aqueous phase.

The practical implications of the process is that brief microwaving or treatment with radiofrequency energy draws out the VOCs from the wood, which can then be collected when the small amount of steam released is condensed (Banerjee et al., 1999). The vapor pressure of α -pinene at 100°C is 0.14 atmospheres (TRC, 1989), which means that 1.2 g of pinene should be removed with every gram of steam. The VOC-depleted wood can then be dried with much-reduced control costs. Although both RF and thermal heating are able to remove VOCs, RF is far

more efficient. Terpenes are driven out from the low-headspace vessel when the small amount of steam is vented, and should be recoverable when the steam is condensed. Heavier organics such as resin acids remain in the vessel. Irradiation did not induce any significant deterioration in strength. It is important to recognize that the wood is *not* dried with electrical energy, but merely maintained at a set temperature for a short period. Thus the high electric power costs typically associated with microwave or radiofrequency drying are not incurred.

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References

1. Alexiou, P.N., A.P. Wilkins and J. Hartley. 1990. Effect of pre-steaming on drying rate, wood anatomy and shrinkage of regrowth *Eucalyptus pilularis* Sm., Wood Sci. Technol. 24,103-110.
2. Anonymous. 1995. Method 25A - Determination of total gaseous organic concentration using a flame ionization analyzer, 40CFR Part 60, 870-872, August 1, 1995.
3. Banerjee, S., M. Hutten, W. Su and L. Otwell. 1995. Release of water and volatile organics from wood drying, Environ. Sci. Technol. 29, 1135-1136.
4. Banerjee, S., W. Su, M.P. Wild, L.P. Otwell, M.E. Hittmeier and K.M. Nichols. 1998. Wet line extension reduces VOCs from softwood drying. Environ. Sci. Technol. 3, 1303-1307.
5. Banerjee, S., J. Boerner, and W. Su. 1999. Method for lowering the VOCs emitted during drying of wood products, US patent pending.
6. Bikales, M. and L. Segal. 1971. Cellulose and cellulose derivatives, Part IV, Wiley, New York.
7. Cronn, D.R., S.G. Truitt and M.J. Campbell. 1983. Atmos. Environ., 17, 201-211.
8. Gordeev, G., A. Maslennikov, M. Ioelovitch and Y. Grunin. 1991. Investigation of the interrelationship between cellulose degree of crystallinity and parameters of free induction NMR signal. Chim. Drev. (Wood Chem.), 3, 27-30.
9. Grzanka, R. PaperAge, April 1996. Facing the EPA cluster rules: the RTO option for emission control. pp. 14-15.
10. Matros, Y.S., G.A Bunimovich, S.E. Patterson and S.F. Meyer. 1996. Catalysis Today, 2, 307-313.
11. Method 25A - Determination of total gaseous organic concentration using a flame ionization analyzer. 40CFR Part 60, 870-872, August 1, 1995.
12. Jeffries, R. 1964. The amorphous fraction of cellulose and its relation to moisture sorption. J. Appl. Polym. Sci., 8, 1213-1220.
13. Krassig, H. 1984. Structure and reactivity of cellulose fibres. Papier, 38, 571-582.
14. Krassig, H. 1977. New structural studies on cellulose fibers using methods of molecular characterisation: infra-red spectroscopy. Lenzinger Ber., 43, 141-151.
15. Krassig, H. 1979. Papier, 33, V9-20.
16. Kamide, K., K. Okajima, T. Matsul, and K. Kowsaka. 1984. Study on the solubility of cellulose in aqueous alkali solution by deuteration IR and 13-C NMR. Polymer J., 16, 857-866.
17. Mann, J. and H.J. Marrinan, 1956. The reaction between cellulose and heavy water: Part I. A qualitative study by infrared spectroscopy. Trans. Faraday Soc., 52, 481-497.

18. National Forest Products Association. 1986. National Design Specifications, Appendix Q. 87
19. Su, W., H. Yan, S. Banerjee, L.P. Otwell, and M.E. Hittmeier. 1999. Field-proven strategies for reducing VOCs from hardwood drying, *Environ. Sci. Technol.*, in press.
20. TRC Vapor Pressure Database, 1989. Texas Thermodynamic Research Center, College Station, TX.
21. Yeo B. 1993. Regenerative Unsteady State Catalytic Oxidation: An Emerging Technology for VOC Oxidation, AIChE Annual Meeting, St. Louis, Missouri.

